X-ray transitions for studying the electronic structure of 5d metals

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Transition metals of the 5d-series, their alloys and compounds are used in a wide range of applications. Unfortunately the direct study of their electronic structure by means of soft X-ray emission spectroscopy is limited due to the absence of suitable X-ray transitions. According to XPS measurements [1], the 5d transition elements (from Hf to Au) have $4p_{1/2,3/2}$ ($N_{2,3}$) core levels in the binding energy region of 380-643 eV. The X-ray emission bands of these metals, arising from the electric dipole transitions between the 5d valence electrons and 4p core level vacancies ($5d \rightarrow 4p_{3/2,1/2}$ transition) can be used for studying the occupied density of 5d-states (DOS). Due to the presence of strong competing radiationless transitions, these spectra are not listed in systematic studies of soft X-ray emission bands of 5d-transition metals [2, 3]. Due to the inherently low fluorescence yield of the ultra-soft x-ray emission process, we utilized the high brightness available at Lawrence Berkeley National Laboratory's Advanced Light Source for the measurements of fluorescence $N_{2,3}$ X-ray emission spectra (XES) of 5d metals. The spectra were taken at Beamline 8.0, employing the soft x-ray fluorescence endstation [4]. Photons with an energy of 399-490 eV, were used for excitation. All measurements reported here were made with a 100-micrometer entrance slit for the spectrometer.

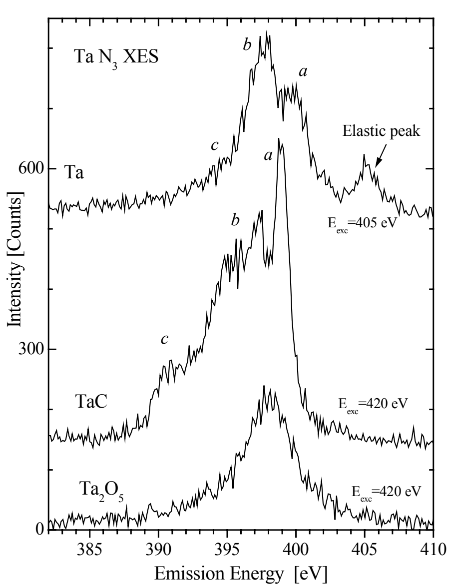

Fig. 1 (a) Ta N_3 XES of Ta, TaC and Ta_2O_5.

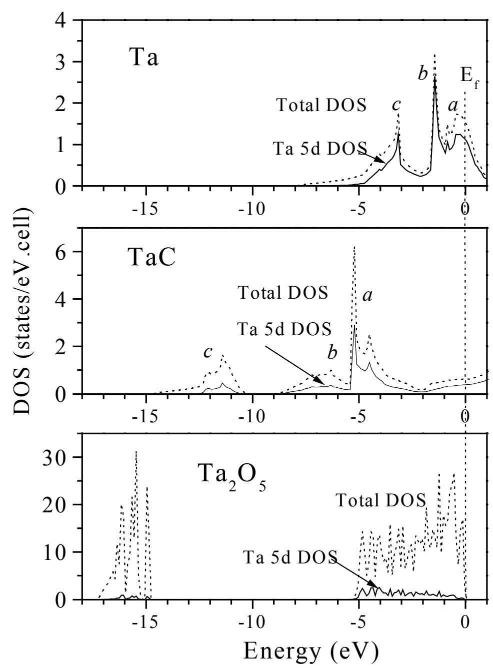

Fig. 1 (b) Total and Ta 5d DOS

We succeeded in measuring non-resonant 5d-metal N_3 ($5d \rightarrow 4p_{3/2}$ transition) soft X-ray emission spectra for Ta, TaC and Ta_2O_5 [5]. The measurements are displayed in Fig. 1(a). X-ray emission is governed by the dipole selection rule, $\Delta l = \pm 1$, which allows only for d- or s-valence electrons to fill the p-type core holes in 5d atoms. The intensity of $N_{2,3}$ non-resonant X-ray emission spectra of 5d elements maps the d-density at the atomic site, or in a band structure picture, the contribution of partial d-type density of states. The measured spectra have a signal to noise ratio of about 10 and show different spectral shape for metal, carbide and oxide evidencing the sensitivity to chemical bonding. According to band structure calculations [5] displayed in Fig. 1b, the main features of Ta 5d DOS are the same as in the total DOS and different in pure metal, carbide and oxide. Ta 5d DOS in pure metal have three subbands (*a-c*) and occupy less energy range than that of TaC. Ta 5d DOS in TaC are strongly hybridizing with the C 2p band giving rise to the structures labeled (*a* to *b*). The additional subband labeled *c* is due to hybridization with C 2s-states. The rather complicated band structure of TaC is reflected in Ta N_3 XES. The energy position of calculated and experimental peaks is in reasonable agreement though the ratio of peaks is rather different. In the case of tantalum pentoxide (Ta_2O_5), the band structure calculations show simpler structure because all Ta 5d electrons occupy the O 2p-band and the d-like band is empty (metal atoms have d^0 configuration). Therefore only the O 2p–Ta 5d band and the atomic-like O 2s-band are present in the valence band of Ta_2O_2. In good agreement with the calculated spectrum, the Ta N_3 emission is of simpler structure for Ta_2O_5 than for TaC. O 2s-states are not seen in Ta N_3 XES of Ta_2O_5 because they are more localized than the C 2s-states and less hybridized with Ta 5d-states.

$5d \rightarrow 4p$ transitions seem to be more favorable for studying the electronic structure of 5d-metals than $5d \rightarrow 5p$ and $5d \rightarrow 4f$ transitions, which are present in the ultra-soft region of 20-90 eV [3]. The reason is that the corresponding metal N_3 X-ray emission spectra are less influenced by core-level vacancies due to the higher localization of 4p-levels compared to 5p and 4f-levels. Therefore one can measure the undistorted density of 5d states.

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